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AMMRC CTR 72-10

PPQ RESIN SYSTEMS FOR HIGH-TEMPERATURE COMPOSITE MATERIALS

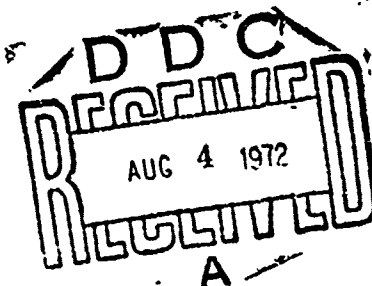
June 1972

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Final Report - Contract DAAG46-72-C-0048

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TECHNICAL
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Prepared for

ARMY MATERIALS AND MECHANICS RESEARCH CENTER
Watertown, Massachusetts 02172

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FOREWORD

This report was prepared by Whittaker Research and Development Division, San Diego, California under Contract DAAG46-72-C-0048. This work was performed under the sponsorship of the Army Materials and Mechanics Research Center, Watertown, Massachusetts during the period 12 November 1971 to 12 April 1972. Mr. Richard T. Rafter and Dr. Walter P. Fitzgerald, Jr., were the principal investigators at Whittaker, assisted by J. M. Shoemaker and C. E. Fox, Senior Fabrication Technicians, and D. R. Thompson, Chemical Technician. The Project Officer for the program at AMMRC was Dr. Gail Mulligan.

This project has been accomplished as part of the U.S. Army Manufacturing Methods and Technology Program, which has as its objective the timely establishment of manufacturing processes, techniques or equipment to insure the efficient production of current or future defense programs.

This technical report has been reviewed and is approved.

ABSTRACT

The subject program has been directed toward the development of the high-temperature resin system, polyphenylquinoxaline (PPQ), based on 3,3'-diaminobenzidine (DAB) and 4,4'-oxybisbenzil (OBB), through the use of a designed trifunctional crosslinking mechanism to provide a unified cured resin system with requisite thermomechanical capability as a laminating resin for end-use application in advanced weapons systems, under the ABM, and related programs.

Initially, removal of residual amine moieties from the linear PPQ system by end-capping with excess OBB provided a readily-processable resin from m-cresol, which produced an excellent Modmor-II unidirectionally reinforced laminate which displayed the highest room-temperature flexural strength to date for any PPQ-based resin system, namely 301,300 psi, with a modulus of 15.3×10^6 psi. This composite displayed, however, the residual thermoplasticity (when tested at 700°F) typical of the linear PPQ resin systems.

On the other hand, trifunctionally cured WRD X-361 PPQ homopolymer has demonstrated complete retention of RT-flexural performance (strength/modulus = 182,000-188,000 psi/ $18.5-18.8 \times 10^6$ psi) in Modmor-II flat laminates at 700°F. This laminate was fabricated using an accelerated cure schedule, attaining a final temperature of 950°F within 1.5 hours and postcuring at that temperature for 0.5 hour. This streamlined cure-postcure schedule has proven necessary to provide more complete cyclization to phenylquinoxaline moieties prior to the onset of macrocyclic resin immobilization in the composite, to upgrade thermomechanical performance of the PPQ resin system.

The incorporation of WRD X-361 as a comonomer in the PPQ polymerization reaction was conducted over a range of loading levels from 0% to 100% X-361. Each of these copolymer resin compositions could be readily fabricated into Modmor-II laminates exhibiting room temperature flexural strengths in excess of 200,000 psi. Again, the accelerated cure schedule was effective in decreasing residual thermoplasticity at elevated temperatures. Thus, laminates fabricated from PPQ resin containing X-361 trifunctional comonomer were shown to retain a higher percentage of initial flexural properties after heat aging than the linear PPQ system using comparable cure conditions.

The use of dimethylacetamide (DMAC) as an impregnation solvent for laminating applications has resulted in a much more facile prepregging operation due to enhanced solubility (ca. 30% solids, vs 15-16% in m-cresol). This enhanced solubility has been translated into improved filament winding capability for the resin system, with a useful level of resin pickup. An excellent demonstration NOL ring was fabricated from continuous Modmor-II fiber and PPQ/DMAC containing 24% X-361 on the initial attempt. Excellent flat composites were fabricated from this DMAC solvent-based system that compared favorably with laminates fabricated from m-cresol PPQ prepolymer solutions.

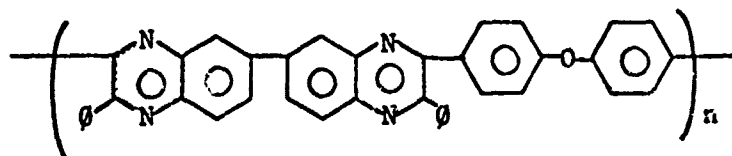
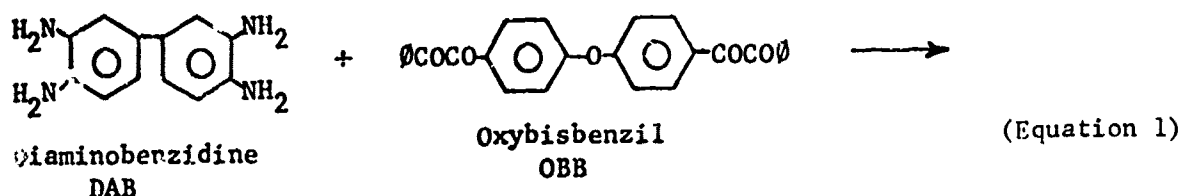
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SECTION I INTRODUCTION

Under the subject contract, Whittaker Research and Development (WRD) has been concerned with the development of the high-temperature polyphenylquinoxaline (PPQ-O) resin system, through controlled cure based on a designed trifunctional phenylquinoxaline cure. The specific linear polyphenylquinoxaline (PPQ) structure employed has been the oxygenated PPQ-O system, prepared from 3,3'-diaminobenzidine (DAB) and 4,4'-oxybisbenzil (OBB) as shown below in Equation 1.



II. Oxygenated Polyphenylquinoxaline
PPQ-O

Under this program, the effectiveness of removing residual amine sites during the linear polymerization by replacing 10% of the OBB monomer with benzil was employed. This "capped" PPQ-O polymer produced an excellent Modmor-II unidirectionally-reinforced laminate which displayed the highest room-temperature flexural strength obtained to date for any PPQ-based composite, namely:

Flexural Strength: 301,300 psi
Flexural Modulus: 15.3 x 10⁶ psi

All of the essentially linear PPQ systems based on 3,3'-diaminobenzidine (DAB) tend to soften above ca. 600°F, limiting their thermal-mechanical performance. This feature severely limits their structural load bearing capacity above these temperatures and, consequently, constitutes the most critical problem yet to be solved for the aromatic heterocyclic polymers. The WRD trifunctional X361 PPQ homopolymer has demonstrated complete retention of RT-flexural performance in Modmor-II flat laminates during testing at 700°F. This laminate had been cured a total time of only 2 hours, including a brief one-half hour exposure to 950°F. This data is shown below.

	Flexural Strength, psi/Modulus, psi x 10 ⁶	
	RT	700°F
Laminate No. 305-11 (100% X-361)	182,100/18.52	187,800/18.83

The residual thermoplasticity of the linear PPQ-O system is perhaps best shown (Table I, Entry A below) by the behavior of a linear PPQ Modmor-II carbon fiber-reinforced laminate in flexural testing at RT and 700°F. During the course of the current program, improvements in these flexural values have been attained through the use of a trifunctional tris-benzil to chemically crosslink the PPQ resin system during cure. The clear superiority of this approach with its abbreviated cure cycle is shown in Table I, Entry B.

TABLE I
THERMOMECHANICAL PERFORMANCE OF
PPQ-O/Modmor-II UNIDIRECTIONAL LAMINATE

<u>Laminate A:</u> Resin: Linear PPQ-O			
Cure: 4 hr @ 750°F, air			
Postcure: RT ~ 300°F in 1 hr, 300°F to 750°F @ 8.4°F/hr, + 12 hr @ 750°F, N ₂			
<u>Laminate B:</u> Resin: 30% X-361 Crosslinked PPQ-O			
Cure: 0.5 hr @ 600°F, air			
Postcure: 0.5 hr @ 950°F, N ₂			
<u>Flexural Strength (psi/Modulus (psi x 10⁶))</u>			
<u>Laminate</u>	<u>RT</u>	<u>700°F after 50 hr @ 700°F</u>	<u>% Strength Retention</u>
A	247,100/16.7	48,800/5.2	20
B	205,300/16.6	73,800/12.3	36

As is evident from the limited data in Table I, the chemically-crosslinked PPQ-O approach has been well vindicated. Thus, the system responds to a more moderate cure cycle, to produce a higher percentage retention of flexural properties after 50 hr aging at 700°F. It remains, however, for supplemental efforts, to define the best method of obtaining full tris-benzil utilization, even to the employment of an alternative, more extended, tris-benzil structure, for increased mobility during cure-postcure, for use in the PPQ-O system for maximum retention of flexural properties at 700°F.

Also, during the course of the current program, it has been found possible to reproducibly fabricate laminates over a wide range of loading levels of X-361 (15-100%), each with room temperature flexural strengths readily exceeding 200,000 psi (see Table II). When laminates of these compositions were cured to only 750°F, however, residual thermoplasticity

remained, as evidenced by thermoplastic deformation of specimens when tested in flexure at 700°F. This program has shown that thermoplasticity can best be eliminated by either a) higher curing temperatures for short periods of time, and/or b) higher loading levels of X-361 in the PPQ system.

TABLE II
TRIFUNCTIONAL PPQ-O COPOLYMER LAMINATES

Copolymer Composition (X-361:OBB)	Room Temperature Laminate Performance	
	Flexural Strength (psi)	Flexural Modulus (psi x 10 ⁶)
15:85	220,300	15.9
30:70	228,900	18.1
45:55	224,700	17.4
50:50	196,400	18.7
100:0	245,000	16.6

Each of the laminates cited in Table II was fabricated using a two-step prepregging technique, necessary to prevent premature gelation of PPQ prepolymer in the m-cresol solution. Use of dimethylacetamide (DMAC) as a replacement solvent for m-cresol appears to totally preclude the gelation problem and, consequently, allow the use of a single-step prepregging operation. Initial laminates were readily fabricated from PPQ/DMAC homogeneous prepolymer solutions at the 24% and also at the 30% loading levels of trifunctional WRD X-361. A demonstration NOL-ring using continuous Modmor Type II fiber and PPQ-O at a loading level of 24% X-361 in DMAC was successfully wound, with a single impregnation step, on the first attempt. The ring produced displayed an impressive cured resin content of ca. 40%, in contrast to 20-25% maximum resin content from m-cresol. The DMAC-wound ring also showed much higher perfection, attributable to the initial higher prepregging solids, and also to the facility of solvent removal (DMAC, b.p. 165°C, vs. m-cresol b.p. 202°C) during cure. This NOL-ring has been forwarded to the AMMRC project officer, as the first demonstration of high performance filament winding with the PPQ-C system.

SECTION II OBJECTIVES

The primary objectives of this program are:

a) To develop the oxygenated polyphenylquinoxaline (PPQ-O) system, based on diaminobenzidine (DAB) and oxybisbenzil (OBB), as a high-temperature resin with a designed trifunctional phenylquinoxaline cure mechanism for distinctly superior long-term thermomechanical performance in high temperature composites;

b) To evaluate the heat-aging performance of these improved PPQ-O systems, primarily in carbon fiber-reinforced laminates, and also to a lesser degree in structural adhesive samples with stainless steel as primary adherend.

SECTION III TECHNICAL DISCUSSION

1. MONOMER SYNTHESIS

a. Diaminobenzidine (DAB)

Ten pounds of 3,3'-diaminobenzidine (DAB) was obtained from a commercial source (Burdick and Jackson). An aliquot, sent for elemental analysis, showed the following results:

	<u>% C</u>	<u>% H</u>	<u>% N</u>
Calc. for DAB:	67.26	6.59	26.15
Found:	67.07	6.68	26.20

Monomer of this purity has already been established as being pure for production of reproducible, highly-processable, polyphenylquinoxaline (PPQ) prepolymer. A study⁽¹⁾ performed in this laboratory under NOL sponsorship has shown that DAB of this quality produces PPQ of equivalent molecular weight and processability to that from recrystallized DAB.

A comparative 100- μ sample of DAB was supplied by the Upjohn Company, prepared on a pilot-plant scale by the amination of dichlorobenzidine. This material was evaluated in standard PPQ-O polymerizations, and was also found to give a processable PPQ prepolymer. A portion was submitted for elemental analysis:

	<u>% C</u>	<u>% H</u>	<u>% N</u>
Calc. for DAB:	67.26	6.59	26.15
Found:	67.21	6.52	26.05

The current approximate pricing on this Upjohn DAB, prepared by the amination of dichlorobenzidine in laboratory quantities is: \$55.00/lb in 10-lb quantities, and \$50.00/lb in 50-lb quantities,⁽²⁾ as opposed to a price of ~\$50.00/lb for the standard DAB (Burdick and Jackson Laboratories) evaluated above. The Upjohn product price can, however, be expected to drop substantially, once the pilot-plant preparation is in-stream.

b. Oxybisbenzil (OBB)

The bisbenzil monomer, 4'4'-oxybisbenzil (OBB), as received from Research Organic Chemicals (Sun Valley, Calif.), mp 103.0°-106.5°C, gave the following elemental analysis:

	<u>% C</u>	<u>% H</u>	<u>% O</u>	<u>% Se</u>
Calc. for OBB:	77.41	4.17	18.42	0
Found:	76.42	3.96	19.66	0

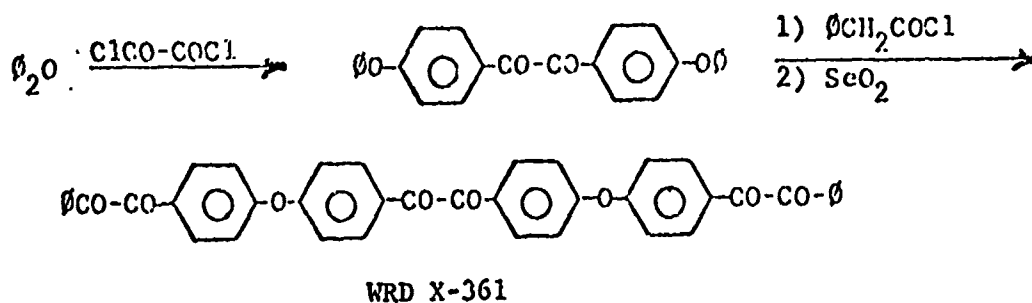
Based on the above results, it was deemed necessary to recrystallize this "commercial" OBB monomer from toluene. A sample of the bright yellow crystalline OBB, after recrystallization, mp 106.5°-108.0°C, gave the following elemental analysis:

	<u>% C</u>	<u>% H</u>	<u>% O</u>
Calc. for OBB:	77.41	4.17	18.42
Found:	77.22	4.05	18.75

This purified OBB was, therefore, used in all polymers for laminating work. (NOTE: Recrystallized OBB, prepared at WRD melts at 106.0°-108.0°C).

c. WRD X-361 Trisbenzil

The synthesis of X-361 co-monomer was carried out, according to the following synthesis scheme*:

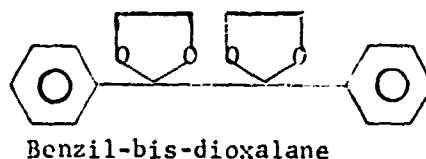


* Structure disclosed for report purposes only. Avoidance of further dissemination is requested.

2. DIOXALANE KETAL DERIVATIVES OF OEB AND OF X-361

Previous studies with m-cresol solutions of free WRD X-361 as co-monomer in the OBB/DAB polymer system, in direct copolymerization attempts, have led to premature crosslinking, resulting in gelation of the polymer during prepregging operations. One approach to circumventing this gelation problem was to synthesize the cyclic ketal derivatives of these reactive benzils, specifically WRD X-361. It was anticipated that these ketals would "block" immediate condensation with DAB to form the quinoxaline until a definite press temperature was attained in laminate form. Complete reaction would thus be attenuated to allow ample time to form workable prepreg. When the layup was then heated during cure, the benzil would be thermally regenerated as to allow complete polymer cyclization. It was, therefore, necessary to determine the comparative reactivity of these cyclic dioxalane ketal modifications of these benzils in a standardized PPQ polymerization.

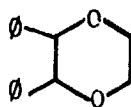
Initially, pending receipt of the 4,4'-oxybisbenzil, the synthesis parameters of the ketal derivatives were evaluated, using benzil itself as a model compound. The usual method of dioxalane synthesis, namely, azeotropic distillation with benzene using p-toluenesulfonic acid catalysis proved ineffective even with extended reaction times at the reflux. Instead, it proved necessary to heat benzil at 140°-160°C in pure ethylene glycol with p-toluenesulfonic acid (HOTS) catalyst. A nitrogen sweep was employed to remove the water. Using this method, the benzil ketal



crystallizes from the ethylene glycol reaction mixture in a pure state, mp 185°-186°C, upon cooling. The infrared spectrum of the isolated product was consistent with the proposed structure for the bis-dioxalane structure. This product yielded the following elemental analysis:

	<u>% C</u>	<u>% H</u>
Calc. for $C_{18}H_{18}O_4$:	72.47	6.08
Found:	72.25	6.16

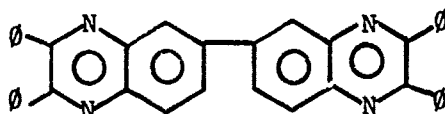
This compound is most likely the above "normal" dioxalane ketal rather than a 1,4-dioxane,



Alternate 1,4-Dioxalane
Derivative

since 1,2-diketones usually give only minor amounts of such a dioxane structure. (3)

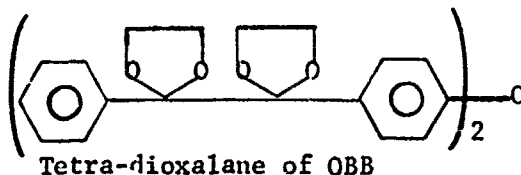
This benzil ketal, however, fails to form the quinoxaline when reacted with DAB in either refluxing m-cresol or refluxing hexamethyl-



Bis-quinoxaline from DAB/Benzil

phosphoramidate, as well as in the melt at 250°C, in the presence of water, with or without HOTS catalyst. The hydrolysis of the ketals of 1,2-diketones is reported (4) to be slow, due to electron withdrawal by the adjacent ketal group. Most of the problem in this case, however, is more likely a competitive acid-base reaction of DAB with the HOTS. The remaining m-cresol is apparently not sufficiently acidic to catalyze the desirable in-situ hydrolysis, even at high temperatures. Ketal hydrolysis is specifically hydronium-ion catalyzed and insufficient hydronium-ion is apparently available in the presence of DAB, to provide a measurable rate of hydrolysis. This reasoning has been experimentally substantiated when benzil ketal was first hydrolyzed to benzil in hot m-cresol with water and HOTS in several minutes. Subsequent treatment of this reaction mixture with excess DAB provided the quinoxaline.

By a route analogous to that used for the preparation of the above benzil ketal, oxybisbenzil (OBB) was treated with excess ethylene glycol and HOTS to give the corresponding tetra-ketal of OBB in 63% yield.



The white crystalline product displayed a melting point of 201°-203°C after recrystallization from dioxane-water.

Several methods were attempted, in order to hydrolyze this OBB ketal (in the presence of DAB), so as to provide lamination processability. These attempts included conducting the reaction in refluxing m-cresol and also in the melt. As expected, based on a corresponding lack of reactivity under similar reaction conditions of the corresponding model compound, benzil itself, in the presence of diaminobenzidine, the OBB ketal was also found to resist acid-catalyzed hydrolysis.

Based on the cost required to pursue this unpromising approach, and in light of the encouraging laminates prepared by the two-step prepregging operation, work with the dioxalane modification to the polymer system has been suspended.

Based on the cost required to pursue this unpromising approach, and in light of the encouraging laminates prepared by the two-step prepregging operation, work with the dioxalane modification to the polymer system was suspended midway in the program.

3. LAMINATING STUDIES

A. Reinforcement Considerations

Lamination studies carried out on this program have centered in the use of meter-length Modmor-II unidirectional reinforcement, employed at a spacing of 5 tows/inch in the prepreg. This Modmor Type II fiber has typically provided the best response among available reinforcements, with respect to both handling characteristics, and also to high flexural strengths. It does however, appear to be more subject to oxidative weight loss at 700°F in air, relative to other available high strength/lower modulus carbon fibers, at least in some cases. This weight loss appears to be a function of laminate void content, as well as of polymer oxidative sensitivity.

Pilot laminates for resin/cure/postcure evaluation have been 4.0 inch x 4.0 inch x 9 plies. A larger mold has been recently employed, 6.0 inch x 4.0 inch, to provide larger laminates, with twice as many flexural specimens as obtainable from a 4.0 inch x 4.0 inch laminate, while requiring only 50% more resin. Resin contents are typically in the 30-35% (w/w) range.

B. Benzil-terminated PPQ-O

The first group of laminates were fabricated from linear, amine-terminated DAB/OBB PPQ polymer that had been subsequently "capped" with benzil itself. This procedure was utilized to evaluate the effect of removing all amine (-NH₂) terminations that could serve as initiation sites for potential oxidative degradation.

One of these laminates (No. 305-1) (10% benzil capped) when cured only 1 hr @ 600°F gave the highest flexural strength obtained to date from this system at room-temperature, namely, 301,300 psi, with 15.3×10^6 psi modulus. As can be seen from Table III, below, that, the benzil-capping leads to complete thermoplastic behavior in flexural testing at 700°F.

TABLE III

BENZIL-CAPPED PPQ-O LAMINATE DATA

Laminate No.	% Benzil Capped	Size, inches/plies	Cure	Flexural Strength (ksi)/ Modulus (psi x 10^6)	
				RT	700°F
305-1	10	4.0x4.0/9	1 hr @ 600°F	301.3/15.3	Not tested
305-3	10	4.0x4.0/9	4 hr @ 700°F	200.6/17.3	11.6/1.3*
305-4	5	4.0x4.0/9	4 hr @ 700°F	241.5/19.3	3.2/0.8*

* Thermoplastic failure.

C. Effect of Crosslinking Agent

Subsequent laminates were fabricated from PPQ-O resin, in m-cresol, containing various loading levels of X-361 to evaluate the effectiveness of the trifunctional tris-benzil in reducing such thermoplasticity at elevated temperature. Each of these laminates were fabricated using the two-step prepregging technique, from m-cresol.

This two-step prepregging method involves withholding the X-361 tris-benzil co-monomer from the m-cresol prepolymer solution to thus prepare an amine-capped prepolymer by reacting the remaining mole-percentage of the OBB benzil with the full stoichiometric complement of DAB tetramine. In every case a prepreggable polymer solution in m-cresol was obtained, which could be readily applied to the Modmor-II fiber layup. After impregnating the prepolymer solution uniformly into the fiber layup, with a "squeegee", a solution of the remaining benzil, X-361, in m-cresol, was dispersed evenly onto the prepreg to balance polymer stoichiometry and allow the resin advancement to proceed on the fiber. These prepreg sheets were then warmed to enhance impregnation, then transferred to a teflon-fabric-covered drying board, dried 20 min at 250°F and cut to laminate size.

The bulk of laminates prepared under this program were fabricated using the above technique. From the data presented in Table IV, it is obvious that the two-stage polymerization procedure used to prepare the chemically-crosslinked laminates is as capable of producing high-perfection, low-void composites as is the stringent thermal cure necessary to prepare laminates from the linear PPQ-O resin with reduced thermoplasticity.

Each of the laminates in Table IV were fabricated using the two-step prepregging technique on meter-length Modmor-II. The prepreg was dried 20 minutes per side at 250°F in a circulating air oven. It was then cut into nine, 4.0 inch x 4.0 inch plies and placed in a steel trap mold with aluminum foil barriers on top and bottom. This layup was then placed in a hot 600°-750°F press and cured. Table IV shows the cure cycle for each laminate and subsequent test data.

TABLE IV

PRELIMINARY PPQ-O (X-361) LAMINATE DATA

Laminates: 4.0 inch x 4.0 inch x 9 plies
 Reinforcement: Modmor Type II, meter length
 Resin Contents: 31-33% (calc.)

Laminate No.	% X-361 Crosslinking Agent	Pressure (psi)	Cure Cycle	Flexural Strength (psi)/ Modulus (psi x 10 ⁶)	
				RT	700°F after 5 min Soak @ 700°F
305-6	15	300	1 hr @ 700°F 1 hr @ 850°F	107,300/15.2	12,100/2.5*
305-5	30	500	1 hr @ 750°F 1/2 hr @ 850°F	228,900/18.1	15,800/1.4*
305-7	45	500	1 hr @ 750°F 1-1/2 hr @ 850°F	224,700/17.4	26,900/5.2*
305-2	100	500	1 hr @ 600°F 4 hr @ 750°F	245,000/16.6	*
305-10	100	500	In 750°F press, 1/2 hr @ 750°F	211,500/16.5	34,800/6.2*

* Thermoplastic failure

All 700°F-test specimens displayed some thermoplastic failure, although initial indications show a favorable response by the resin to both an increase in cure temperature (850°F) and to an increase in the loading level of X-361. With the exception of Laminate No. 305-6, cured at a lower pressure, all of the above initial laminates were of high perfection, as evidenced by the high values of RT-flexural performance obtained.

As can be seen in Table IV (Laminate No. 305-2) above, even the 100% WRD X-361/DAB laminate has not been fully cured after 4 hr @ 750°F, as evidenced by the thermoplastic failure at 700°F. Laminates with lower loading levels of the trifunctional X-361 component, when the composites are given brief exposures to cure temperatures at 850°F, still gave evidence of residual thermoplasticity. Since a thermal decomposition temperature * of 1000°F has been reported⁽⁵⁾ for the aryl ether linkage (possibly the thermally weakest link in the PPQ-O backbone), it was deemed necessary to utilize brief exposures at higher cure temperatures to preclude polymer degradation while removing this residual thermoplasticity.

Both of the last two laminates in Table IV (Laminates No. 305-2 and 305-10) were fabricated from 100% WRD X-361/DAB homopolymer PPQ system. Laminate No. 305-2 was cured 1 hr @ 600°F, followed by a 4-hr cure @ 750°F. A test specimen from this composite was too thermoplastic at 700°F for flexural testing. A similar composite, Laminate No. 305-10, however, also fabricated from 100% WRD X-361/DAB PPQ, was cured only 0.5 hr @ 750°F (in hot press at 750°F) with no precure. This composite, while still somewhat thermoplastic at 700°F, gave a flexural strength of 34,800 psi at that temperature. It was felt that attainment of higher cure temperatures (deemed necessary to remove residual thermoplasticity as discussed above) as rapidly as possible should permit greater mobility in the polymer system during the curing cycle to completely cyclize all remaining reactive moieties and attain the maximum crosslink density. It is possible, for example, that full cyclization has not been achieved during the precure cycle at 600°-750°F. Instead, after only partial cure, the resin matrix may have gelled, thereby preventing full PPQ polymer M.W. advancement during the high temperature cure/postcure due to immobilization. P. J. Flory has discussed this premature gelation of trifunctional-curing polymers at length.⁽⁶⁾

D. Effect of Cure Cycle

It was necessary, therefore, to evaluate: 1) the effectiveness of higher cure temperatures, and 2) the effect of streamlining the cure cycle with rapid achievement of final cure temperature vs. typical gradual step-wise postcure. These parameters were preliminarily evaluated using two laminates, each with 30% loading of WRD X-361. Cure cycles and test data are shown below in Table V for these two comparative laminates.

* Temperature at which a decomposition rate of 1% per hour is observed.

TABLE V

PPQ-O LAMINATE DATA

(Rapid Temperature Rise to High Curing Temperature Evaluation)

Laminates:	4.0 inch x 4.0 inch x 9 plies				
Reinforcement:	Modmor Type II, meter length				
Resin:	PPQ-O, 30% X-361 crosslinked				
Laminate No.	Calc. Resin Content (%)	Pressure (psi)	Cure Cycle	Flexural Strength (psi) / Flexural Modulus (psi x 10 ⁶) 700°F after 5 min soak @ 700°F	Wt. Loss (%) 700°F after 50 hr @ 700°F
305-8	33	500	1 hr @ 650°F, air 1/2 hr @ 650°F, N ₂ 1 hr @ 750°F, N ₂ 1 hr @ 850°F, N ₂ 1 hr @ 900°F, N ₂ 1/2 hr @ 950°F, N ₂	RT 148,900/17.7 135,800/18.1 10,700/5.0	20.2
305-13	27	500 100	1/2 hr @ 650°F, air 1-1/2 hr @ 950°F, N ₂	205,300/16.6 161,600/16.5 73,800/12.3	8.5

As can be seen in Table V, the protracted (5 hr) cure cycle applied to laminate No. 305-8 was sufficient to remove the thermoplasticity during initial 700°F testing. These incompletely cyclized residues remaining, however, apparently caused substantial degradation during 50 hr aging at 700°F, as evidenced by the decreased flexural values after the heat aging. In the comparison laminate (Laminate No. 305-13), however, the resin was apparently able to achieve full cyclization prior to resin immobilization, by the accelerated cure rate to 950°F. The result was an excellent composite, with no evidence of thermoplastic deformation during flexural testing at 700°F, when cured a total time of only 2 hours. This singular composite also gave the best flexural strength at 700°F after 50 hr @ 700°F for this crosslinked PPQ-O system to date (73,800 psi).

A subsequent laminate, containing WRD X-361 at a loading level of 100%, was fabricated using the accelerated cure schedule. This laminate (No. 305-11) was also cured for a total time of 2 hours; there was no loss of flexural properties of this laminate when tested at 700°F over the values obtained at RT. Data from this composite are shown below in Table VI.

Flexural properties after 50-hr heat aging at 700°F had decreased significantly from initial, to approximately one-half the value obtained after similar heat-aging on a 30% trifunctionally-cured laminate. This difference can most logically be attributed to laminate irregularities, or to differences in actual cure-response, on a single-laminate comparative basis, rather than to inherent resin deficiencies.

TABLE VI

THERMOMECHANICAL PERFORMANCE OF WRD X-361 HOMOPOLYMER

Laminate No.	Size, inches/plies	Cure	Flexural Strength, ksi/ Flexural Modulus (psi x 10 ⁶)		
			RT	700°F	700°F after 50 hr @ 700°F
305-11	4.0x4.0/9	1/2 hr @ 750°F	182.1/	187.8/	39.4/5.1
		1 hr @ 900°F	18.52	18.83	
		1/2 hr @ 950°F			
		Wt. Loss	--	--	13.9%

Table VII summarizes all of the laminates prepared from m-cresol solutions of PPQ-O polymer systems.

TABLE VII

PRQ-O LAMINATE SUMMARY
Reinforcement: Modmor-II

Laminate No.	X-361 Loading Level (%)	Calc. Resin Content (%)	Pressure (psi)	Cure Cycle	Flexural Strength, ksi/Modulus, psi x 10 ⁶		
					RT	700°F	700°F after 50 hr @ 700°F (wt. loss)
305-1	0 ⁽¹⁾	30	500	1 hr @ 600°F	301.3/15.3	--	--
305-2	100	35	500	1 hr @ 600°F 4 hr @ 750°F	245.0/16.6	*	--
305-3	0 ⁽¹⁾	32	500	4 hr @ 700°F	200.6/17.3	*	--
305-4	0 ⁽²⁾	--	500	4 hr @ 700°F	241.5/19.3	*	--
305-5	30	31	500	1 hr @ 750°F 1/2 hr @ 850°F	228.9/18.1	15.8/1.4*	--
305-6	15	--	300	1 hr @ 750°F	107.3/15.2	12.1/2.5*	--
305-7	45	32	500	1 hr @ 750°F 1-1/2 hr @ 850°F	224.7/17.4	26.9/5.2*	--
305-8	30	33	500	1 hr @ 650°F 1/2 hr @ 650°F, N ₂ 1 hr @ 750°F, N ₂ 1 hr @ 850°F, N ₂ 1 hr @ 900°F, N ₂ 1/2 hr @ 950°F, N ₂	148.9/17.7	135.8/18.1	10.7/5.0
305-9	100	35	500	4 hr @ 750°F 3 hr @ 850°F, N ₂	128.4/12.8	44.3/6.5	--
305-10	100	34	500	1/2 hr @ 750°F	211.5/16.5	34.8/6.2*	--
305-11	100	31.2	500	1/2 hr @ 750°F 1 hr @ 900°F, N ₂ 1/2 hr @ 950°F, N ₂	182.1/18.5	187.3/19.8	30.4/5.1(13.9)
305-12	60	26.5	500	1/2 hr @ 600°F 1-1/2 hr @ 950°F, N ₂	124.9/18.0	77.7/17.3	Burnt out (20.9)
305-13	30	27.3	500 100	1/2 hr @ 600°F 1-1/2 hr @ 950°F, N ₂	205.3/16.6	161.6/16.5	73.8/12.3(8.5)
305-14	45	--	500 100	1/2 hr @ 600°F 1 hr @ 950°F, N ₂	135.0/17.0	92.5/16.1	--
305-16	30	26	500 100	1/2 hr @ 600°F 1 hr @ 950°F, N ₂	109.0/17.3	51.0/5.5*	--
305-19	0 ⁽³⁾	23	500 100	1 hr @ 600°F 1 hr @ 900°F, N ₂	238.7/19.9	26.9/6.0	--
					Beam Shear, psi RT 700°F		
					7410	5510	--
					Initial 600°F after 200 hr @ 600°F (wt. loss)		
					45.1/10.2	60.4/13.7(5.0)	4120

(1) 10" benzil capped

(2) 5" benzil capped

(3) 2" benzil capped

* Thermoplastic failure.

E. PPQ-O/DMAC Resin System

Contemporaneous IR&D developmental work aimed at applications such as wet-spinning, where a water-miscible solvent is required, performed at WRD has shown that the linear PPQ-O system can be prepared in, and also dissolved to a solids concentration of 50% in dimethylacetamide (DMAC) solvent. This solvent system has been consequently applied to this current program and has provided a high-quality laminates. An example of the flexural values obtained from a linear (0% X-361) PPQ-O composite fabricated from a DMAC prepregging solution using the brief, accelerated cure schedule is shown below in Table VIII.

TABLE VIII

PPQ LINEAR RESIN COMPOSITE DATA

Reinforcement: Modmor-II

Laminate No.	Size. inches/plies	Cure Schedule	Flexural Strength, ksi/ Modulus, psi x 10 ⁶	
			RT	700°F
2173-9	4.0x4.0x10	500 psi, 1 hr @ 600°F	210.4/18.4	210.7/18.9
		100 psi, 1 hr @ 950°F		

This solid modification has permitted the fabrication of low-void composites with excellent flexural properties, while avoiding the higher boiling point and difficulty of removal of the incumbent m-cresol solvent system, during polymer preparation, prepregging and laminating operations, and, most importantly, during cure and postcure.

Extension of the DMAC solvent technology from the linear PPQ-O resin to the X-361 crosslinked PPQ-O resins was also found possible. Thus, it has recently been found possible to formulate X-361-crosslinked PPQ-O resin at both the 24%- and also the 30%-loading levels into single homogeneous prepolymer solutions that are most readily processable. This breakthrough is significant, not only for the direct replacement of m-cresol, but also for removing the necessity for two-stage prepregging operations. Also, composite hardware prototypes of advanced designs can be filament-wound from a single, homogeneous prepolymer solution, avoiding possible errors in stoichiometric pickup from a two-part prepregging solution.

Initial flat laminates have been prepared from the PPQ-O copolymer resin at the 24% and 30% loading levels in single, homogeneous solutions in DMAC. Data from these preliminary laminates are shown below in Table IX.

TABLE IX

PPQ-O/X-361 COPOLYMER LAMINATES FROM DMAC PREPOLYMER SOLUTION

Laminate No.	% X-361	Cure Schedule	Resin Content (%)	Void Content (%)	Flexural Strength, ksi/ Modulus, psi x 10 ⁶	
					RT	700°F
2173-3	30	500 psi, 1 hr @ 675°F 100 psi, 1 hr @ 950°F, N ₂	29.0	14.3	160.7/16.02	14.6/1.72*
2173-5	24	500 psi, 1/2 hr @ 675°F 100 psi, 1 hr @ 950°F, N ₂	27.5	5.1	167.0/16.5	37.1/6.4*

* Thermoplastic failure

Although further development is required to totally remove thermoplastic behavior at 700°F, and also to reduce composite void content, it is now obvious that DMAC should be considered the preferred solvent for PPQ-O polymer/prepregging solutions, providing that ultimate thermomechanical performance is not found to be adversely affected. Thus, as can be seen from Table IX, above, even a PPQ-O Modmor-II composite of over 14% void content gave a respectable room-temperature flexural strength and modulus of 160,700 psi and 16.02 x 10⁶ psi respectively.

The real significance of this effort was realized when a demonstration NOL-ring was successfully fabricated on the first attempt from a homogeneous PPQ-O/X-361 prepolymer solution, at a loading level of 24% trifunctional component, at the 30% resin solids level in DMAC. Resin pickup on the continuous Modmor-Type II fiber was 46% with remaining volatile content of 18% on the prepreg tape. An excellent NOL-ring was thus fabricated and cured at 800°F. The cured ring had a calculated resin content of 40%.

This encouraging lead must, therefore, be pursued in supplemental developmental work of this, or alternate, PPQ-O resin systems. A schematic of the NOL-ring filament-winding train is shown in Appendix I.

SECTION IV CONCLUSIONS AND RECOMMENDATIONS

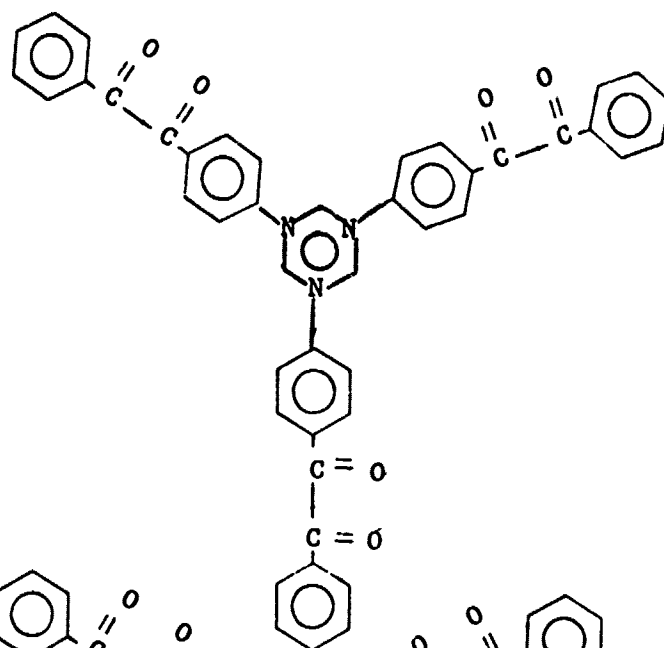
The use of DMAC as a solvent for the PPQ-O/X-361 copolymer resin system has greatly enhanced its processability by providing a more ready release of reaction volatiles, higher solids content in prepolymer solution, and avoidance of the requirement for two-stage prepregging technique operations, necessary with m-cresol solvent. Initial flat laminates and, subsequently, an NOL ring, were dense, with negligible void content, when fabricated from DMAC prepolymer solutions. It is clearly evident that DMAC should be considered the preferred solvent for future trifunctionally cured PPQ-O resin systems.

Also, the streamlined cure/postcure (to 850°-950°F) approach has led to the production of flat laminates which retain ca. 100% of RT flexural strength when tested at 700°F. Heat-aging performance after 50 hours @ 700°F, however, has been improved, but can be expected to improve further by modification in trifunctional component structure and/or cure-postcure schedule. The same level of retention (ca. 50% of RT-values) of flexural strength after 50 hours @ 700°F has been obtained from this system as has been realized with the oxygen-free PPQ system DAB-PGB PPQ. Since the PPQ-O/X-361 system contains far more aryl ether linkages per mer unit, it is reasonable, therefore, that this (Ar-O-Ar) linkage is not the prime cause of oxidative degradation during heat aging at 700°F. Rather, molecular immobilization as a result of quinoxaline cyclization during a too rapid cure can be anticipated to leave residual Schiff-base linkages which deteriorate during heat aging. Further credence in this hypothesis has been found with improved performance after a streamlined cure-postcure, designed to avoid this immobilization to a large extent.

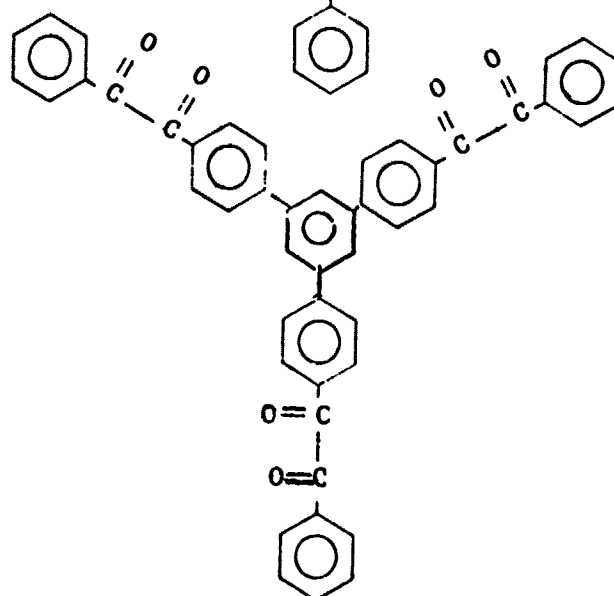
It is, therefore, proposed to consider an investigation of more mobile (extended) tris-benzils to develop a more efficient cyclization during cure to render the thermomechanical performance of the PPQ-O system equivalent to its isothermal aging capability. Such an investigation should comprise the first phase of a concerted supplemental effort toward most-readily accessible tris-benzils and should include the synthesis of the most accessible tris-benzils (cf. below). All of these tris-benzil candidates (a-c, below) utilize trifunctional intermediates, already synthesized in our laboratories.

NOTE: The triphenyl-s-triazine nucleus (the center of structure a) when incorporated as the residual inter-chain linkage in the trifunctional poly(imidazoquinazoline) (PIQ) homopolymer resin system has provided ca. 100% retention of thermomechanical (flexural) properties after 100 hr heat aging at 700°F. Similar response can thus be readily anticipated in the thermally-stable PPQ-O system.⁽⁷⁾

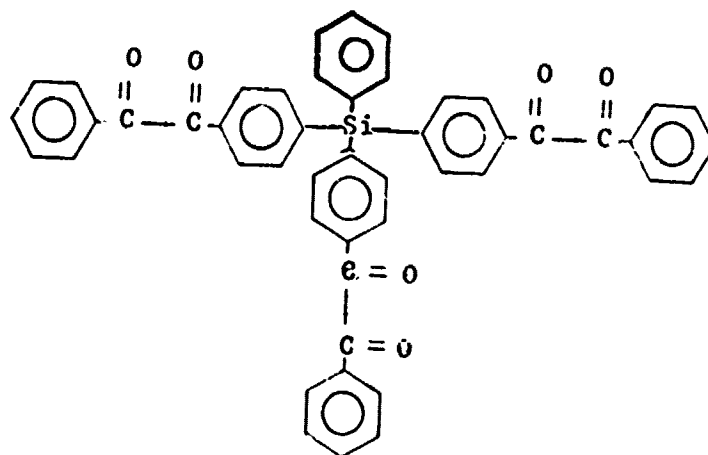
a)



b)



c)

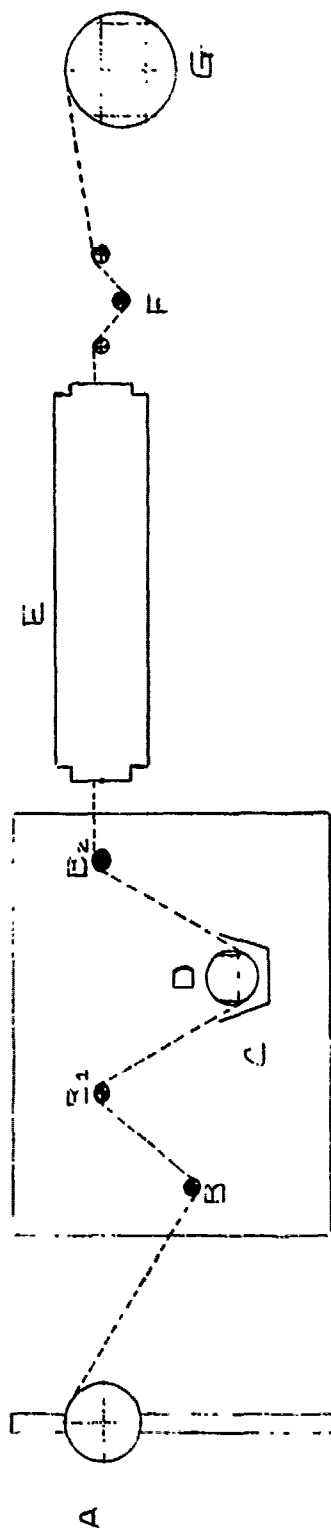


REFERENCES

- (1) R. T. Rafter and W. P. Fitzgerald, High Temperature Polymer Development, Annual Report, Contract N60921-69-C-0073, Whittaker Research and Development Division, San Diego, California, Dec 1970.
- (2) C. W. Stewart, Upjohn Company, Manager, Commercial Development, personal communication to W. P. Fitzgerald, Jr.
- (3) A. I. Cohen, I. T. Harper and S. D. Levine, Chem. Comm. 1610 (1970).
- (4) R. H. Jaeger and H. Smith, J. Chem. Soc., 160 (1955).
- (5) I. B. Johns, E. A. McElhill and J. O. Smith, Jour. of Chem. and Eng. Data, 7, 277 (1962).
- (6) P. J. Flory, Principles of Polymer Chemistry, Chap. IX, Cornell University Press, Ithaca, New York, 1953.
- (7) W. P. Fitzgerald, R. J. Milligan, and B. Y. Sanders, Exploratory Development of High Temperature Resins, Final Report, Contract No. F33615-71-C-1544, Whittaker Research and Development Division, San Diego, Calif., June 1972.

APPENDIX I

PPQ NOL-Ring Winding Apparatus



A Modmor II continuous fiber

B } Fiber guide rollers
B₁
B₂

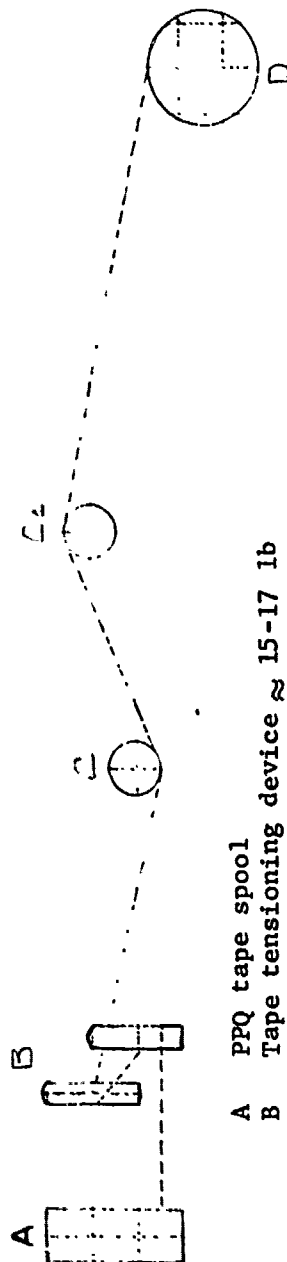
C Dip tank (30% resin solution in DMAC)

D Grooved roller

E Tube furnace 300°C

F Graphite guides

G Tape take-up spool



A PPQ tape spool

B Tape tensioning device ≈ 15-17 lb

C } Tape guide rollers 0.200 in. groove
C₁

D Electrically heated tool ~ 750°F